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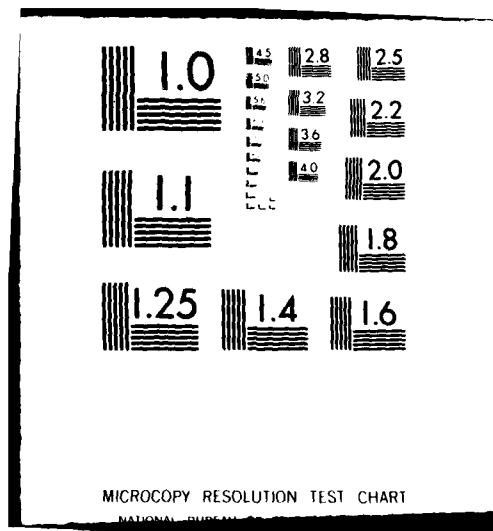
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THE ADSORPTION AND ELECTROOXIDATION OF SIMPLE HYDROCARBONS FOR --ETC(U)
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THE ADSORPTION AND ELECTROOXIDATION OF SIMPLE HYDROCARBONS
FOR DIRECT OXIDATION HYDROCARBON-AIR FUEL CELLS, (U)

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JUN 1980

INTRODUCTION

The development of new and more sophisticated tactical weapon systems mandates that reliable electrical power sources are also available. The ideal tactical power source should be silent, lightweight and mobile. A fuel cell system would meet these requirements. Hydrogen-air fuel cells are now being considered for deployment for the near future. In order to obtain hydrogen rich mixtures for fuels, these fuel cell systems must be equipped with one of the following: hydrogen storage devices, thermal crackers, steam reformers, or partial oxidizers. A direct oxidation hydrocarbon-air fuel cell would be more attractive, since it would eliminate the above items and result in a lighter, less complex system. A fuel cell system, which could operate interchangeably on a variety of fuels, would be an added benefit. This report describes the research effort at MERADCOM to develop such a system. The overall objective is to provide the basic information required for the development of a direct oxidation hydrocarbon-air fuel cell.

A fuel cell is an electrochemical system which converts the free energy of a chemical reaction between a fuel and an oxidant directly to electrical energy. The electrochemical path of a saturated hydrocarbon in a fuel cell may be summarized as shown in Figure 1. A hydrocarbon is adsorbed on the anode to form an adsorbate by a reaction as shown in either 1-a or 1-b. The adsorbate is subsequently oxidized according to reaction 2 to yield carbon dioxide, hydrogen ions and free electrons. These electrons can flow through an external circuit to the cathode where they react with oxygen as

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shown in reaction 3. If no side reactions occur, the overall electrooxidation process is as shown by reaction 4. However, important problems have persisted in developing efficient catalysts for these reactions. Even on platinum, one of the best catalysts available, the rate of fuel oxidation has been less than that possible under mass transfer control. It was the specific objective of this research to make a mechanistic study of the anode reaction in hopes of finding the key to improving the reaction kinetics.

PROBABLE REACTION PATH FOR HYDROCARBON OXIDATION

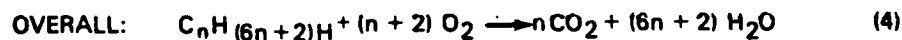
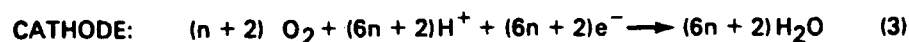
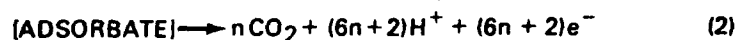
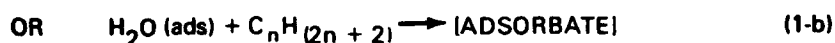
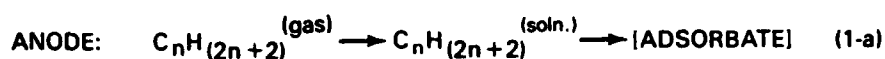


Figure 1. Probable reaction path for the electrooxidation of a saturated hydrocarbon.

Earlier studies(1,2,3,4) have shown that hydrocarbons adsorb and form carbonaceous species on platinum electrodes at potentials greater than 0.1 V vs Reversible Hydrogen Electrode (RHE). Brummer^(5,6) has shown that these species can be classified in three general types which he labeled as CH- α , CH- β and O-type. He discounted the CH- β specie as an active participant in the overall oxidation or reduction. This left the CH- α and O-type for consideration. The role of these species in the overall oxidation reaction has been discussed by Brummer⁽⁸⁾. The observation by Adams and Barger⁽⁹⁾ that higher rates of propane oxidation were attained in trifluoromethanesulfonic acid opens the possibility that these species are influenced by the electrolyte. Therefore, this investigation was undertaken to compare the amounts of these adsorbates in two electrolytes. Since the electrode is an important component in a fuel cell, two electrode structures were also compared.

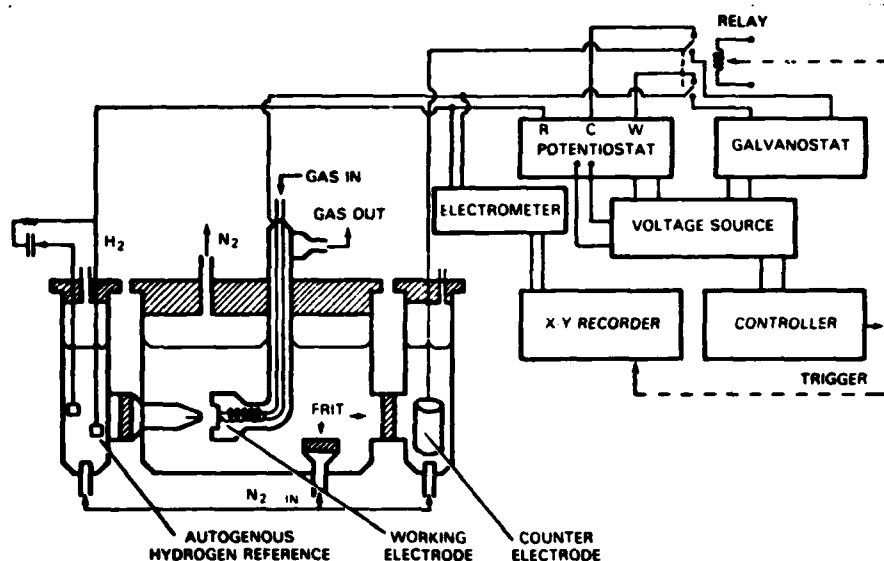


Figure 2. The electrochemical cell and controls.

EXPERIMENTAL

Apparatus and Materials. The electrochemical cell and control circuitry are shown in Figure 2. The cell was a conventional three compartment half-cell normally used in electrochemical investigations. Each compartment is continuously flushed with humidified nitrogen to expel oxygen from the electrolyte. The counter electrode was a high surface area platinized platinum screen. The reference electrode was the autogenous hydrogen electrode described by Giner⁽⁷⁾ and was 10 mv cathodic to the reversible hydrogen electrode. Two types of Teflon-bonded gas diffusion fuel cell electrodes were used as the working electrodes. One contained 4 mg/cm² of platinum-black as the catalyst while the other used carbon-supported platinum with a loading of 0.62 mg Pt/cm² as the catalyst. A circular section of the electrodes was mounted in a Teflon holder which also served as the gas supply.

The electrolytes were phosphoric acid and trifluoromethanesulfonic acid (TFMSA). The phosphoric acid was treated with hydrogen peroxide and solutions of the desired compositions were made by adding distilled water. The TFMSA was distilled and the

fraction between 160 - 161°C was retained for dilution. The solutions were pre-electrolyzed prior to use with a high surface area platinized platinum electrode which was potentiostated at 0.4 V vs RHE for 16 hours.

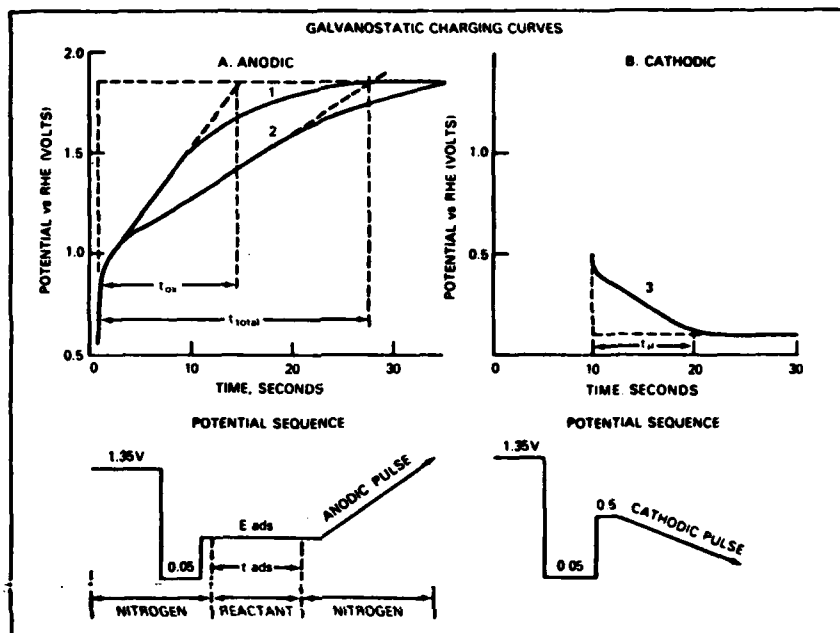


Figure 3. Potential sequences and resulting charging curves.

Experimental Procedures. The experimental procedure is similar to the galvanostatic method devised by Brummer, Ford and Turner. It consists of using a sequence of potentiostatic and galvanostatic pulses to measure surface coverages and amounts of reactants adsorbed. The potential sequences and resulting curves are diagrammed in Figure 3. The electrode is held at a potential where any impurity or previously adsorbed material is oxidized, usually 1.35 V vs RHE, and followed by a potentiostatic pulse to 0.5 V vs RHE to reduce the oxide film and leave a clean surface for adsorption. The electrode is then raised to the potential of interest (E_a) and the reactant allowed to adsorb for a specified time. After removing the excess reactant, an anodic galvanostatic pulse is applied to oxidize the adsorbate. The time required to anodically oxidize the electrode and adsorbate (t_{TOTAL}) can be followed by recording the potential vs time (trace 2, Figure 3).

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When no reactant is present, only the electrode is oxidized and a background curve is obtained (trace 1). Using these curves, the time required to oxidize the adsorbate (t_A) can be computed from

$$t_A = t_{\text{TOTAL}} - t_{\text{ox}}$$

Since the applied current (i) is known, the amount of adsorbate can be computed in terms of the oxidizable charge (Q_A) required to remove the adsorbate.

$$Q_A = i \times t_A$$

A similar sequence of potentials is used with a cathodic pulse to obtain a curve as shown by trace 3. This curve follows the adsorption of hydrogen atoms on the platinum electrode. From the adsorption time (t_H), the charge for depositing hydrogen atoms (Q_H) can be computed. The surface area of the electrode was computed by assuming a monolayer of hydrogen corresponds to 210 $\mu\text{coul}/\text{cm}^2$. Unless otherwise stated, all measurements are referred to this area. The fraction of surface covered by the hydrocarbon material is also measured using a cathodic galvanostatic pulse. The ratio of t_H obtained after adsorption to t_H obtained from a clean electrode under helium gives the fraction of surface occupied by hydrocarbon atoms (θ_H). The fraction covered by the hydrocarbon is $(1 - \theta_H)$. The general background for this method has been discussed earlier.(2)

Current-voltage curves were measured by potentiostating the electrode at the adsorption potential with the reactant flowing through the gas cavity until steady-state was reached, usually about 10 minutes, and the current recorded. Background curves were measured over the same potential range and subtracted from the current data.

RESULTS AND DISCUSSION

The efficiency of a hydrocarbon-air fuel cell is highly dependent on the adsorption characteristics and oxidation kinetics of the organic molecule used for fuel. Several investigators have examined the oxidation of organic molecules under electrochemical conditions.(2,3,4) Of general interest is propane because of its availability and relatively low cost. Earlier studies with propane adsorbed on solid electrodes have shown that the mechanism involves the dissociation of the molecule into a number of fragments which

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immediately adsorb on the electrode surface. The evidence indicates that the adsorbate is composed of several carbonaceous species in various states of oxidation. The nature of these species and their possible roles in the overall reaction scheme has been discussed previously. (6,8) There is the likelihood that the most highly oxygenated specie is the most preferred in terms of ease of subsequent oxidation to carbon dioxide. Therefore, it is desirable to determine if the concentration of this specie is affected by the electrolyte medium and the electrode structure.

Several experiments were performed to measure the extent of adsorption of propane and methane on platinum electrodes from phosphoric acid and trifluoromethanesulfonic acid electrolytes. Galvanostatic charging curves were used to estimate the amount of adsorbate formed as a function of potential at steady-state coverage on platinum-black and carbon-supported platinum fuel cell electrodes. The amount of adsorbate was measured in terms of the amount of charge per square centimeter required to oxidize the residue. Rates of oxidation, where feasible, were also measured for each electrode-electrolyte system. A number of preliminary experiments were performed for each electrode-electrolyte system, where the adsorption time was varied and the amount of residue measured, to determine when steady-state was reached. The time of maximum adsorption was a function of potential up to about 5 minutes, but in all cases, it was attained after 10 minutes. All additional steady-state experiments were carried out for this time.

Two types of residues were observed, one cathodically desorbable and another which could only be removed by strong oxidation. The cathodically desorbable residue has been labeled as the CH- α and is probably in a highly reduced state. The cathodically non-desorbable residue is considered to be a combination of the previously mentioned CH- β and O-type species.

Adsorption of Propane. The total amount of residues adsorbed from the steady-state adsorption of propane as a function of potential is shown in Figure 4. Maximum adsorption is observed from 14.7 M H_3PO_4 onto platinum-black electrodes. Comparing electrolytes of equal acid strength, i.e., 5.6 M H_3PO_4 and 5.6 M $\text{CF}_3\text{SO}_3\text{H}$, more adsorption occurs on the platinum-black with $\text{CF}_3\text{SO}_3\text{H}$ as electrolyte. At the more cathodic potentials, beyond 0.3 V, more propane is adsorbed on the carbon-supported platinum electrode than on the platinum-black electrode from H_3PO_4 , although it is slightly less than that adsorbed onto platinum-black from $\text{CF}_3\text{SO}_3\text{H}$. Measurements of the surface coverage of the total adsorbate were not possible

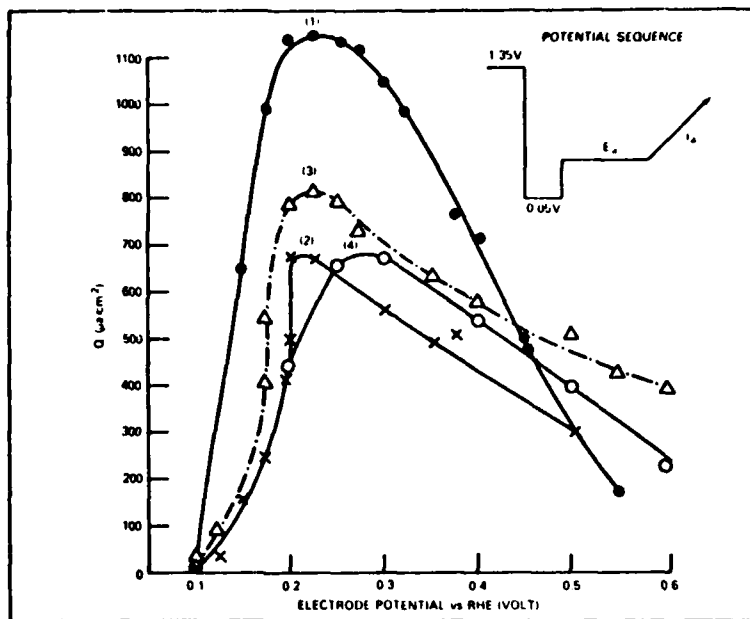


Figure 4. Total propane adsorbate vs potential;
 (1) Pt-blk - 14.7 M H₃PO₄, (2) Pt-blk - 5.6 M H₃PO₄,
 (3) Pt-blk - 5.6 M CF₃SO₃H, (4) Pt-C - 5.6 M H₃PO₄.

since the CH- α species are rapidly desorbed following application of the cathodic galvanostatic pulse. This is not the case with the cathodically non-desorbable species and the amounts adsorbed along with the surface coverage were measured for these species. These data are shown in Figures 5 and 6. Examination of these plots show that generally there is increased adsorption from the CF₃SO₃H and onto the carbon-supported platinum electrodes. There is also an increase in the accumulation of the cathodically non-desorbable residue. The maximum coverage is observed for platinum-black from CF₃SO₃H with approximately 50% of the surface covered between 0.4 and 0.6 V. The carbon-supported electrodes required approximately the same amount of charge to oxidize the residues, but they had much less coverage. The anodic and cathodic data were further used to characterize this residue. From the ratio of Q_A to $(1 - \theta_H)$ (210×10^{-6}) the number of electrons, $[e]$, per occupied site of platinum required to oxidize the residue to CO₂ was estimated. These data are summarized as a function of potential for each electrode-electrolyte system in Table 1. The values for the phosphoric acid/

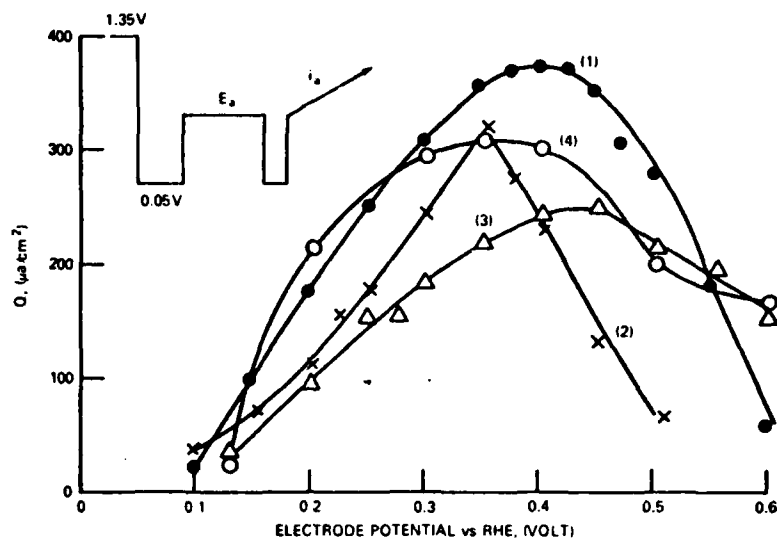


Figure 5. Cathodically non-desorbable propane adsorbates vs potential; (1) Pt-blk - 14.7 M H_3PO_4 , (2) Pt-blk - 5.6 M H_3PO_4 , (3) Pt-blk - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$, (4) Pt-C - 5.6 M H_3PO_4 .

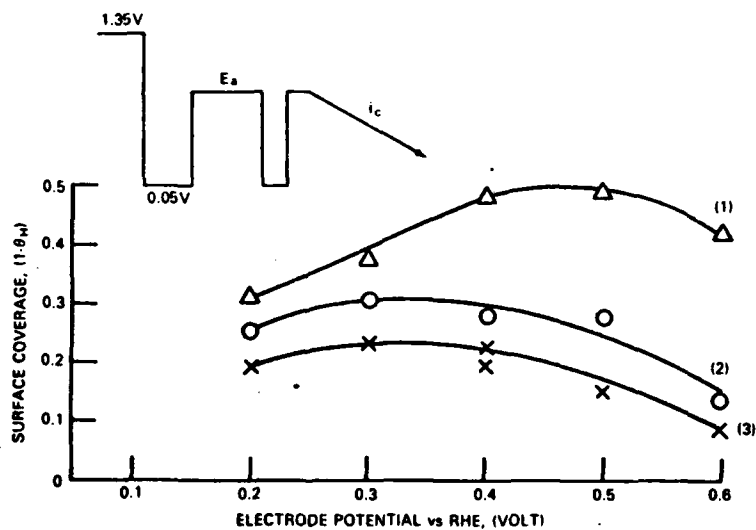


Figure 6. Surface coverage of cathodically non-desorbable propane adsorbates vs potential; (1) Pt-blk - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$, (2) Pt-C - 5.6 M H_3PO_4 , (3) Pt-C - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$.

Table 1. Average Number of Electrons Per Occupied Site of Platinum for Non-Desorbable Adsorbates of Propane and Methane						
Adsorbent	Electrode Potential (Volt)	Average Number of Electrons/Site				
		14.7 M H ₃ PO ₄ Pt-blk	5.6 M H ₃ PO ₄ Pt-blk	5.6 M CF ₃ SO ₃ H Pt-blk	5.6 M H ₃ PO ₄ Pt-C	5.6 M CF ₃ SO ₃ H Pt-C
C ₃ H ₈	0.2	2.3	2.0	1.5	6.7	2.1
	0.3	3.0	3.7	2.2	6.6	3.6
	0.4	3.5	3.7	2.3	6.6	5.3
	0.5	2.8	6.0	1.9	3.7	6.5
CH ₄	0.2	2.5		2.2		
	0.3	3.3		1.7		
	0.4	2.8		2.1		
	0.5	2.7		2.5		

platinum-black system range from 2-4 while the values for the tri-fluoromethanesulfonic acid/platinum-black system averaged about 2 at all potentials. The low values of $[e]$ suggest a highly oxidized specie; for example, a value of 2 would indicate a CO specie. The higher values observed for carbon-supported platinum in both electrolytes infers that the residue contains species which are in a more reduced state. It is also possible that these electrodes contain a mixture of adsorbates with different oxidation states. Although not clearly definitive, the evidence indicates that both the electrode and electrolyte affects the adsorption characteristics of propane.

Adsorption of Methane. Methane adsorbs to a lesser extent than propane in all cases. The adsorption and fractional coverage as a function of electrode potential are summarized in Figures 7 and 8 respectively. No cathodically desorbable residues were detected from the adsorption of methane. Several similarities between the non-cathodically desorbable residues from the adsorption of propane and the residues from methane are noted. The amounts of surface residues and coverage varies with the electrode potential and is greater in CF₃SO₃H than in H₃PO₄. The amounts adsorbed on the carbon-supported platinum is greater than on platinum-black. The average number of electrons is also 2-3 per platinum site. This observation indicates that the molecular species comprising the residue could be the same as the cathodically non-desorbable adsorbate formed from propane.

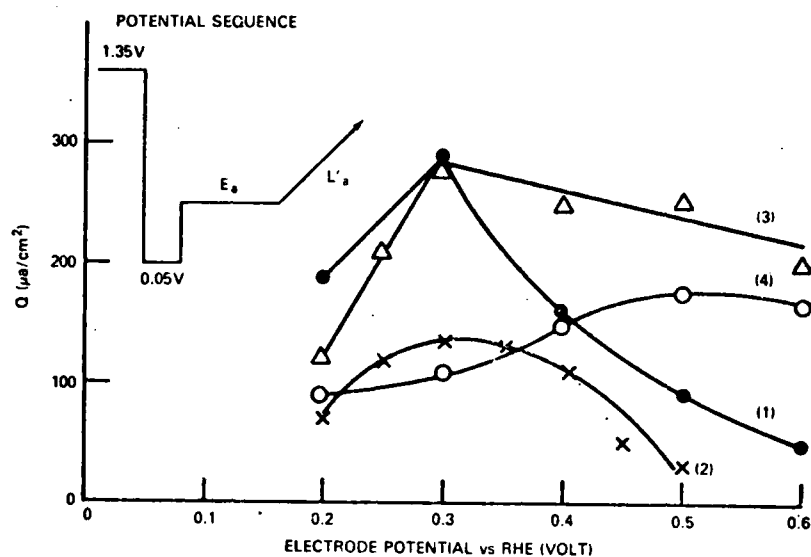


Figure 7. Methane adsorbate vs potential; (1) Pt-blk - 14.7 M H_3PO_4 , (2) Pt-blk - 5.6 M H_3PO_4 , (3) Pt-blk - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$, (4) Pt-C - 5.6 M H_3PO_4 .

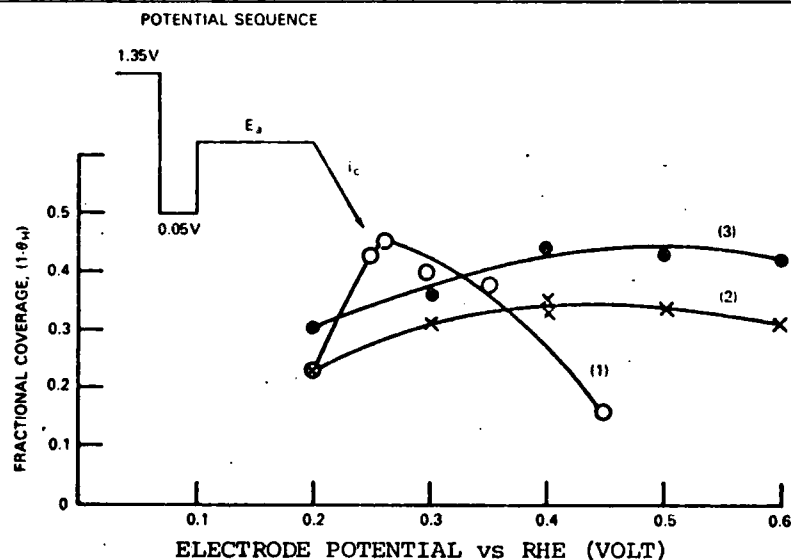


Figure 8. Fraction coverage of methane adsorbate vs potential; (1) Pt-blk - 14.7 M H_3PO_4 , (2) Pt-C - 5.6 M H_3PO_4 , (3) Pt-C - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$.

Rates of Oxidation. Figure 9 shows the steady-state potential-current density plots of the two electrode structures with propane and methane in H_3PO_4 and $\text{CF}_3\text{SO}_3\text{H}$. The electrooxidation rate is greater in $\text{CF}_3\text{SO}_3\text{H}$ than in H_3PO_4 for the same electrode structure while the platinum-black electrode has a greater oxidation rate than carbon-supported platinum in the same electrolyte. The limiting current density for propane in 5.6 M $\text{CF}_3\text{SO}_3\text{H}$ on carbon-supported platinum is $15 \mu\text{a}/\text{cm}^2$ while the value on platinum-black is $27 \mu\text{a}/\text{cm}^2$. Only $3 \mu\text{a}/\text{cm}^2$ was observed for platinum-black in 14.7 M H_3PO_4 . This represents a substantial increase when it is considered that the temperature was 25°C in the former case and 80°C in the latter.

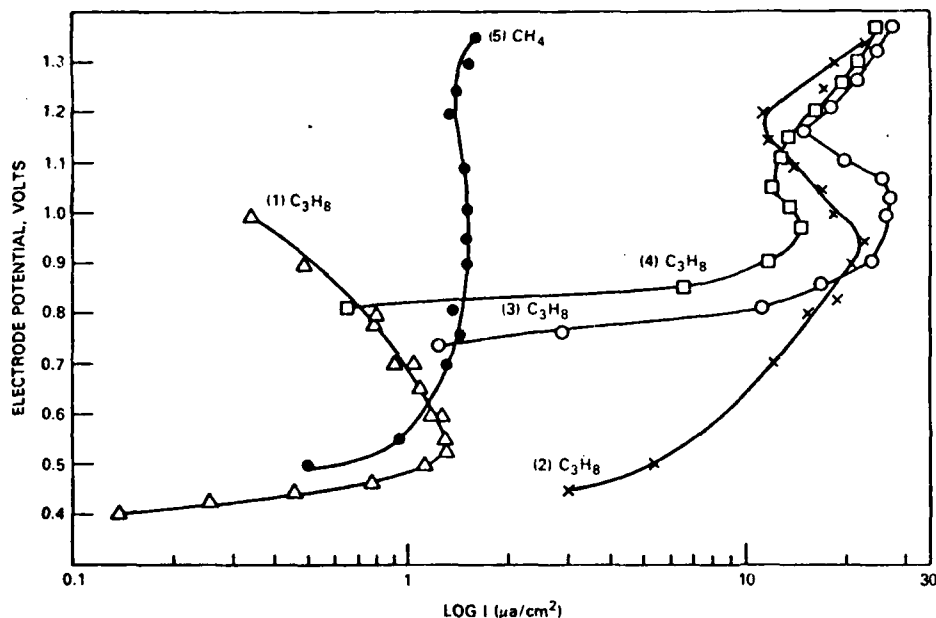


Figure 9. Potential-current density curves for steady-state electrooxidation of methane and propane; (1) Pt-blk - 14.7 M H_3PO_4 , (2) Pt-C - 5.6 M H_3PO_4 , (3) Pt-blk - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$, (4) Pt-C - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$, (5) Pt-blk - 5.6 M $\text{CF}_3\text{SO}_3\text{H}$.

SUMMARY AND CONCLUSION

The findings from this investigation are summarized as follows:

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(1) Hydrocarbons are adsorbed on practical fuel cell electrodes in a similar manner as on solid electrodes. The amount adsorbed at steady-state is potential dependent.

(2) Propane produces two types of adsorbates, one which is cathodically desorbable. Methane residues contained only one molecular specie, which is similar to the O-type from propane.

(3) Increased adsorption was observed in trifluoromethanesulfonic acid than in H_3PO_4 . Higher oxidation rates were also obtained in the former electrolyte.

(4) Increased adsorption was measured on the carbon-supported platinum electrodes although the adsorbates on these electrodes were in a more reduced state than those on platinum-black.

It is concluded that the rate of electrochemical oxidation of simple hydrocarbon molecules is highly dependent on electrolyte environment as well as the catalyst structure. By developing specific catalysts and electrolytes, highly reactive intermediates could be produced which oxidize at rates fast enough to make a hydrocarbon-air fuel cell practical.

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